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EP 0 456 306 B1

Description

Field of the invention

The invention relates to a novel process for making fibres of linear alternating polymers of carbon monoxide and ethylene. The polymer is also referred to as poly(ethyleneketone), polyketone, or poly-(ethene-alt-carbonmonoxide) and it has the following repeating unit in the chain molecule:

$$- CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} -$$

Background of the invention

European Patent Application No. 360 358 describes a process for the preparation of polyketone fibres which are said to be useful as reinforcing material.
The fibres are made by successively spinning a solution of a polyketone, removing the solvent from the obtained fibres, and stretching the fibres at an elevated temperature.
According to the specification and the Examples of European Patent Application 360 358 the solvents advantageously employed for preparing the polymer solution are hexafluoroisopropanol, m-cresol, and mixtures thereof. Moreover, minor amounts of compounds that are non-solvents for the polyketones may be employed in combination with the solvents mentioned hereinbefore. Such compounds include, among others, ketones such as acetone, with ethanol being mentioned as a preferred non-solvent.
International Patent Application (PCT) No. WO 90/14453, published after the priority date of the present application, describes polyketone fibres and a method for the production of such fibres. The fibres are made by successively dissolving the polyketone in a suitable solvent, spinning the solution, removing all or some of the solvent from the spun fibre and stretching the fibre at elevated temperature.
The solvent preferentially used for preparing the spinning solution is chosen from the group consisting of hexafluoroisopropanol, m-cresol, phenol, pyrrole, 2-chlorophenol and 3-chlorophenol. A non-solvent for the polyketone may be used to stimulate the separation of the polyketone from the solvent in the spun object. Suitable non-solvents for this conversion are acetone, methyl ethyl ketone and toluene.
Although the processes of European Patent Application 360 358 and International Patent Application WO 90/14453 may provide polyketone fibres having properties which make them useful for some end-uses, improvements are desired with respect to the cost and the toxicity of the spinning solvents used, the speed of the spinning process, and the mechanical properties of the resulting fibres.

Summary of the invention

The present invention involves a novel spinning process for making fibres of an alternating carbon monoxide ethylene polymer having an estimated molecular weight of at least 100 000 g/mole in which a solution of the polymer in a mixture of solvents, at least one of which is an aromatic alcohol being free of alkyl radical substituents on the aromatic nucleus and another of which is a liquid other than an aromatic alcohol, is extruded into a shaped solvent-containing article at an extrusion rate of at least 1 m/min, after which the article is solidified by cooling or coagulating and the solvent removed from it by extraction with a non-solvent for the polymer which is soluble in the mixture of solvents, whereupon the article is drawn at a temperature of at least 180 °C.

Detailed description of the invention The polymer

The polymer used in the spinning process of the invention is an alternating polymer of carbon monoxide and ethylene. It is highly preferred that the polymer be a pure homopolymer because, in that case, optimum fibre properties are obtained. However, small amounts of other units are acceptable, as long as the polymer molecules consist in essence of chain units of the type:

$$[-\ CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} -\ ]$$

This is the case when the other units are present in an amount which does not exceed 5 mole per cent. Alternatively, it is possible to mix a polyketone with a terpolymer, on the condition that the total mixture does not contain more than 5 mole per cent of units different from the

$$[-\ CH_2 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} -] \text{ - unit.}$$

The polymer is well-known in the art and many processes for making it have been described, e.g. in US Patent 3,689,460. The polymer to be used in the invention should have an estimated molecular weight (MW) of at least 100 000. The estimated molecular weight can be determined by measuring the Intrinsic Viscosity (IV) in a solution of meta-cresol. The Intrinsic Viscosity is also referred to as Limiting Viscosity Number or LVN and is expressed in dl/g. The relation between the estimated molecular weight (in g/mole) and the IV (in dl/g) as measured in meta-cresol at 25 °C can be given by the formula:

$$IV = 1.0 \times 10^{-4} \times MW^{0.85}$$

As is usual with polymer fibres, the tensile properties, especially the tenacity, are more favourable as the MW is higher. Therefore, the aim is to obtain the highest possible MW, but this is subject to practical restrictions in that there are limits as to production and processability. Since making polyketone fibres by use of the process of the invention requires the preparation of a spinning dope, the maximum MW that can be used is about 1 000 000. For practical purposes the preferred polymer has an IV in the range of 2 to 20.

Processes for making the polymers also have been described in European Patent Specifications 121 965; 222 454; 224 304; 227 135; 228 733; 229 408; 235 865; 235 866; 239 145; 245 893; 246 674; 246 683; 248 483; 253 416; 254 343; 257 663; 259 914; 262 745; 263 564; 264 159; 272 728, and 277 695.

The polymers always are a mixture of molecules of different molecular weights, preference being given to those in which the MW distribution is as small as possible.

The process for making polyketone fibres

The spinning process of the invention comprises preparing a dope from the polymer and a special mixture of solvents and subsequently extruding it into elongated structures at a temperature at which it is liquid. Next, the structures are solidified to form solid articles from which the solvent is removed by extraction with a non-solvent for the polymer which is soluble in the dope solvent, after which they are stretched or drawn. When solidification takes place by thermo-reversible crystallization, this process is usually referred to as gel spinning. When it takes place by crystallization due to extraction of the solvent, i.e. coagulation, the process is referred to as wet spinning.
A very efficient spinning process is the so-called air gap spinning process or dry jet-wet spinning process. This process per se is old in the art, having been described as early as 1961, see e.g. Canadian Patent Specification No. 711,166 or French Patent No. 1 327 017.

The dope solvents

Although a great number of organic compounds can be used to dissolve the polymer, most of these cannot be utilized as a dope solvent in the process of the invention. The dope solvent should meet a number of requirements, e.g.:

- low toxicity
- easy to recycle
- not too low boiling point
- not too expensive

- solubility in liquids that can be used as a spinning bath
- stable under the process conditions
- chemically inert in relation to the polymer
- combination with the polymer should give spinnable solutions, i.e. the solutions should contain enough of the polymer for a commercial spinning range, and the crystallization of the polymer from the solvent should be neither too slow nor too rapid.

According to European Patent Application 360 358 and International Patent Application WO 90/14453 hexafluoroisopropanol may advantageously be used as a solvent for spinning polyketones. Although this compound is a very good solvent for the polymer, it is too toxic and expensive for commercial use. Moreover, its use does not result in fibres having the excellent mechanical properties which can be achieved according to the present invention.

Also too toxic for use in actual practice are compounds such as orthochlorophenol and chloropropanol.

European Patent Application 360 358 and International Patent Application WO 90/14453 also disclose meta-cresol as an advantageous solvent. Although this compound, as well as other aromatic alcohols such as phenol, hydroquinone, and resorcinol is a satisfactory solvent, the polymer does not crystallize readily from solutions in these solvents and so their use will lead to spinning speeds which are too low for commercial practice.

Although other compounds such as ethylene carbonate and propylene carbonate can dissolve the polymer at high temperatures, their use is attended with the polymer crystallizing too rapidly and in too coarse a form during cooling, so that the resulting yarns do not have acceptable mechanical properties.

According to the present invention use is made of a process in which a solution of the polymer in a mixture of solvents, at least one of which is an aromatic alcohol being free of alkyl radical substituents on the aromatic nucleus and another of which is a liquid other than an aromatic alcohol, is extruded into a shaped solvent-containing article at an extrusion rate of at least 1 m/min, after which the article is solidified by cooling or coagulating and the solvent removed from it by extraction with a non-solvent for the polymer which is soluble in the mixture of solvents, whereupon the article is drawn at a temperature of at least 180 °C.

Preferably the extrusion rate is at least 3 m/min.

Preferably the article is drawn at a draw rate of at least 5, more preferably of at least 10.

Excellent results were obtained according to the invention with mixtures of

(a) ethylene carbonate or propylene carbonate and

(b) an aromatic alcohol being free of alkyl radical substituents on the aromatic nucleus,

in which the (a):(b) weight ratio is in the range of 1:1 to 19:1.

Preferred aromatic alcohols being free of alkyl radical substituents on the aromatic nucleus are phenol, resorcinol, and hydroquinone.

Other preferred components of the spinning dope are acetone and water.

A most preferred mixture of solvents used for preparing the polymer solution of this invention comprises resorcinol and water. The weight ratio of resorcinol to water in such a mixture may be in the range of from 1:2 to 20:1. Preferably it is in the range of from 2:1 to 5:1.

Other non-aromatic alcoholic liquids that may be used in admixture with the aromatic alcohols are, e.g.:

1,6 hexanediol
1,4 butanediol
benzyl alcohol
di-ethylene glycol
ethylene glycol
glycerol
tri-ethylene glycol
epsilon caprolactam
dimethyl phthalate
dimethyl sulphoxide
phosphoric acid
N-methyl-2-pyrrolidone
alpha pyrrolidone.

The polymer content of the solutions of this invention is generally in the range of from 1 to 50 per cent by weight, preferably in the range of from 5 to 30 per cent by weight.

Crystalline properties

By use of the process of the present invention, fibres can be prepared which have a very high birefringence, The values for the fibres that can be made in accordance with the invention are at least 650.10^{-4}, preferably at least 659.10^{-4}. Optimum fibres have a birefringence of at least 670.10^{-4}. The maximum which can be attained is about 750.10^{-4}.
The extraordinarily high birefringence of the fibres that can be prepared by the process of this invention is related to their unique mechanical properties, i.e. very high initial modulus and tenacity.
Fibre X-ray diffraction photographs can be taken of the fibres of the invention using a precession camera with CuKα radiation.

The process of the present invention makes it possible to make fibres which display a unique crystallographic pattern with d-spacings of the three major reflections at the equator of 4.09-4.13, 3.43-3.49, and 2.84-2.90 Å, and so are to be preferred, since only the homopolymers show major equator reflections in this range.
The fibres prepared by the process of the invention have their crystals arranged mainly in the direction of the fibre axis, which means that the orientation angle (OA) is low.

The fibres consist of a mixture of crystalline and amorphous material. Ideally, fibres should be completely crystalline. Given that the density is affected by the amount of amorphous material, density measurements will give an impression of the crystallinity. By use of the process of the present invention, fibres having a density in the range of 1.25-1.38 g/cm^3 can be prepared. It is preferred to prepare fibres with a density in the upper values in this range, more especially with a density in the range of 1.31-1.38 g/cm^3.

Although the melting point T_m of the homopolymer from which the yarns are made is about 257°C (obviously the inclusion of small amounts of terpolymer will reduce the T_m), the crystalline structure of the yarn preferably is such that it will not melt below 265°C. The special spinning process according to the invention raises the melting point by 4 to 23 degrees Centigrade. The higher the molecular weight of the polymer, the higher the rise in melting point will be. The melting point of the fibres that can be made by use of the process of the invention is an indication of their quality in the sense that a higher melting point represents a higher crystallinity. Preference is given to prepare fibres that have a melting point of from 265° to 280°C, preferably of from 270° to 280°C. The melting point is the peak melting temperature in DSC-thermograms determined with a Perkin Elmer®DSC7 at a scan speed of 20°C/min on samples of pieces of fibre of about 1-5 mg in weight and 1-5 mm in length. The DSC apparatus is calibrated by recording thermograms on Indium test samples.

Properties of the fibres that can be made by use of the process of the invention

By use of the process of the present invention, fibres can be made that have very attractive properties, rendering them suitable for use in industrial applications, for instance as reinforcing yarns for rubber articles such as tyres and conveyor belts. They can also be used in woven or non-woven textiles, for reinforcing roofing membranes, and for geo-textiles. In general, the process of the invention makes it possible to prepare fibres that can replace such conventional industrial yarns as rayon yarns, nylon, polyester and aramid yarns.

The yarns have a high tensile strength. What makes them especially valuable is their high creep resistance, which is not only greatly superior to that of the high-modulus polyethylene yarns but also to that of polyethylene terephthalate yarns.

The fibres made by the process of this invention can be used as filamentary yarns composed of endless filaments, which yarns may be twisted and treated in the usual way with adhesion promotors and other treatments to enhance their properties.
The fibres may also be transformed, with crimping or not, into staple fibres. Alternatively, they can be transformed into pulp by the usual processes known for this purpose. The pulp thus obtained is useful for the reinforcement of friction materials, asphalt, concrete, etc., and as a substitute for asbestos.

Measurements and tests

Inherent Viscosity (IV)

IV is defined by the equation:

$$IV = \lim_{c \to o} \frac{\eta spec}{c}$$

wherein c is the concentration of the polymer solution and η_{spec} (specific viscosity) is the ratio between the flow times t and t_o of the polymer solution and the solvent, respectively, as measured in a capillary viscometer at 25 • C. The solvent used is meta-cresol. The specific viscosity thus is:

$$\eta spec = \frac{t-t_o}{t_o}$$

The IV test is conducted in meta-cresol at 25 • C. The polymer is dissolved by being mixed in the solvent at 135 • C for 15 minutes. The polymer concentration is dependent on the expected IV and is selected as follows:

Expected IV:	chosen concentration:
0 - 0.5	0.2 - 1.0 g/dl
0.5 - 1.0	0.2 - 0.8 g/dl
1.0 - 3.0	0.1 - 0.25 g/dl
3.0 - 5.0	0.07- 0.12 g/dl
> 5.0	0.03- 0.06 g/dl

Fibre properties

Filament properties are measured on fibres that have been conditioned at 20 • C and 65 % relative humidity for at least 24 hours.

Tenacity (i.e., breaking tenacity), Elongation (breaking elongation), and Initial Modulus are obtained by breaking a single filament or a multifilament yarn on an Instron tester. The gauge length for single broken filaments is 10 cm. The results for 3 filaments are averaged. All samples are elongated at a constant rate of extension of 10 mm/min.

The filament count (expressed in tex) is calculated on the basis of functional resonant frequency (A.S.T.M. D1577-66, part 25, 1968) or by microscopic measurement.

The tenacity, elongation, and initial modulus as defined in A.S.T.M. D 2256 - 88, published April 1988, are obtained from the load- part has a cone angle greater-elongation curve and the measured filament count.

The tenacity and initial modulus are expressed in units GPa and mN/tex. For ease of comparison the meaning of these parameters and the relation between them is as follows:

$$1 \text{ GPa} = 10^9 \text{ N/m}^2$$
$$1 \text{ mN/tex} = 10^{-3} \text{ N/tex}$$

$$1 \text{ GPa} = \frac{1000}{\text{density}} \text{ . mN/tex (density of the solid material in g/cm}^3\text{)}$$

The preferred fibres of this invention have a tenacity (T) of at least 1300 mN/tex, more particularly of at least 1500 mN/tex, and an initial modulus (M) of at least 35 N/tex, more particularly of at least 50 N/tex. The elongation at break of the fibres of the invention preferably is in the range of from 2.5% to 10%.
Tex is the number equal to the weight in grams of 1000 m of yarn.
The average values for tenacity and modulus for known yarns are:

Polyparaphenylene terephthalamide:	T = 3 GPa (2100 mN/tex) M = 120 GPa (84 N/tex)
Steel:	T = 2.8 GPa (360 mN/tex) M = 200 GPa (26 N/tex)

Birefringence

The birefringence can be measured in accordance with the method described by H. de Vries in Rayon Revue 1953, p. 173-179. The fibre is immersed in dibutyl phthalate and use is made of light having a wavelength of 558.5 nm. The results of 10 measurements are averaged.

Examples

Use was made of a homopolymer of carbon monoxide and ethylene. The intrinsic viscosity values were determined in meta-cresol at 25 °C. In some of the experiments the tenacity of the obtained fibre is given in GPa (which is the same as GN/m^2); in these cases the cross-section of the fibre was determined microscopically. Where the tenacity is given in mN/tex, the linear density of the fibre was determined with a vibroscope.

In all the examples the polymer was dissolved in the mixture of solvents, with heating and stirring, until a homogeneous solution was obtained. The solution was then placed under vacuum until the gas bubbles had disappeared. At the temperature indicated in Table 1 the spinning dope thus obtained was spun through a spinneret into a spinning bath, as indicated in Table 1. After having been washed free of the dope solvent, the yarn was wound onto a spool and dried. The yarn was then drawn at the temperatures and draw ratios given in Table 1. The properties of the thus obtained yarns are given in Table 2.

The spinnerets used in the examples had:

Example 1:	1 capillary of a diameter of 300
Example 2:	1 capillary of a diameter of 500
Example 3:	1 capillary of a diameter of 500
Example 4:	6 capillaries of a diameter of 250
Example 5:	6 capillaries of a diameter of 250
Example 6:	1 capillary of a diameter of 500
Example 7:	6 capillaries of a diameter of 125

The extrusion and winding rates and the air gap lengths in the examples were as follows:

Example:	Extrusion rate	Winding rate	Air gap length
1	3.24 m/min	0.49 m/min	no air gap
2	1.99 m/min	2.00 m/min	10 mm
3	1.99 m/min	2.00 m/min	10 mm
4	2.99 m/min	3.00 m/min	5 mm
5	2.99 m/min	3.50 m/min	8 mm
6	1.99 m/min	2.00 m/min	10 mm
7	5.70 m/min	0.42 m/min	20 mm

If conditions are not optimal during the manufacturing process the resulting fibres will not, of course, exhibit the high level of mechanical properties in all cases.

Table 1. Spinning conditions

Ex.	Spinning dope	Spinning bath	Drawing temp. °C	Draw ratio
1	1.02 parts polymer of IV=6.1	acetone	a.	1
	12.45 parts phenol	Temp.= -5°C	b. 225	2.5
	1.25 parts acetone		c. 225	3
	T = 20°C		d. 225	4
			e. 225	5
			f. 225	6
			g. 225	7.5
			h. 225	8
			i. 225	10
			j. 225	12.5
			k. 225	12.8
			l. 225	15
			m. 225/250	15
			n. 225	16
			o. 225/250	17.5
			p. 225/250	18
			q. 225/250	20
2	8 parts polymer of IV=6.1	acetone	a. 175/225/250	15
	64.8 parts phenol	Temp.= -4°C	b. 175/225/250	16
	7.2 parts acetone		c. 175/225/260	15
	T = 110°C		d. 175/225/260	16
			e. 175/225/260	17
			f. 225/260	25.5
3	7 parts polymer	acetone	a. 175/225/250	5/2 (total 10)/1.5 (total 15)
	of IV=6.1	Temp.= 10°C	b. ditto	5/2 (total 10)/1.6 (total 16)
	56.7 parts phenol		c. ditto	5/2 (total 10)/1.7 (total 17)
	6.3 parts acetone T = 115°C			
4	7 parts polymer	acetone	225	first step 8
	of IV=5.46	Temp.= -15°C	a. 225/250	total 15
	69.35 parts propylene carbonate		b. 225/250	total 16
	3.65 parts hydroquinone		c. 225/250	total 17
	T = 210°C		d. 225/250	total 18
5	6.4 parts polymer of IV=5.46	acetone	a. 225	5
	43.8 parts propylene carbonate	Temp= -15°C	b. 225/250	10
	29.8 parts resorcinol		c. 225/250	15
	T = 175°C		d. 225/255	18
			e. 225/255	19
			f. 225/256	19

6	10.5 parts polymer of IV=3.89 53.55 parts phenol 5.95 parts acetone T = 115°C	acetone T= -15°C	a. 175/225/260 b. 175/225/260 c. 175/225/260 d. 175/225/260	15 16 17 18
7	7.2 parts polymer of IV=5.46 54.6 parts resorcinol 18.2 parts water T = 100°C	acetone T= -15°C	a. 243/257/260 b. 243	20.4 11.3

Table 2. Fibre properties

Example	Tenacity GPa	In. modulus GPa	Elongation at break %	Birefringence 10^{-4}	T_m °C
1a	0.25	1.9		55	
1b				388	
1c	0.64	9.5	9.6		
1d	0.93	11.0	9.7	533	
1e					
1f	1.20	16.5	9.2	584	
1g					
1h	1.55	20.3	8.9	626	
1i	1.50	22.4	6.9	633	
1j					
1k	1.63	30.7	6.2	665	
1l				670	
1m					269
1n				659	
1o					
1p	1.9	51.2	5.0	685	
1q	2.1	55.0	3.6		
Example	**Tenacity mN/tex**	**In. modulus N/tex**	**Elongation at break %**	**Birefringence 10^{-4}**	**T_m °C**
2a	1271	34.6	4.05	670	271
2b	1335	34.0	4.31		271
2c	1430	33.2	4.57		272
2d	1360	34.8	4.25		273
2e	1354	38.4	3.93	678	272
2f	169.2	58.8	3.2		
3a	1047	21.3	5.04		
3b	1141	23.6	4.98		
3c	1376	31.8	4.67		
4a	952	9.92	7.76		261
4b	1065	12.2	7.32		262
4c	950	13.2	6.35	609	263
4d	1139	15.5	6.46		264
5a	215	3.02	10.10		259
5b	396	4.94	7.93		264
5c	883	9.35	7.62		265
5d	1020	12.0	7.40		265
5e	1172	14.8	7.24		266
5f	976	12.0	6.85	587	267
6a	1470	23.6	6.22	631	264
6b	1449	26.2	5.62		271
6c	1307	29.7	4.70		265
6d	1170	30.6	4.16	665	264
7a	1624	37.0	4.70		277
7b	1048	18.0	5.40		274

From the fibres of three examples WAXD-recordings were taken revealing equator reflections being in accordance with the following d-spacings:

Example	d(110)	d(200)	d(210)
2e	4.110	3.454	2.86
4d	4.107	3.476	2.88
5e	4.109	3.462	2.86

Claims

1. A process for making a high tensile strength and high modulus fibre from a linear alternating polymer of carbon monoxide and ethylene having an estimated molecular weight of at least 100 000 g/mole, characterized in that,
   - a solution of the polymer in a mixture of solvents, at least one of which is an aromatic alcohol being free of alkyl radical substituents on the aromatic nucleus and another of which is a liquid other than an aromatic alcohol, is extruded into a shaped solvent-containing article at an extrusion rate of at least 1 m/min,
   - the article is solidified by cooling or coagulating in a non-solvent for the polymer, and the solvent is removed from it by extraction with a non-solvent for the polymer which is soluble in the mixture of solvents, whereupon
   - the article is drawn at a temperature of at least 180 °C.

2. A process according to claim 1, characterized in that the article is drawn at a draw ratio of at least 10.

3. A process according to any one of the claims 1-2, characterized in that the dope is spun into a fibre in an air gap spinning process.

4. A process according to any one of the claims 1-3, characterized in that the extrusion rate is at least 3 m/min.

5. A process according to any one of the claims 1-4, characterized in that the mixture of solvents comprises (a) ethylene carbonate or propylene carbonate and (b) an aromatic alcohol in which the (a):-(b) weight ratio is in the range of 1:1 to 19:1.

6. A process according to any one of the claims 1-4, characterized in that the aromatic alcohol is resorcinol

7. A process according to any one of the claims 1-4, characterized in that the liquid which is not an aromatic alcohol is acetone.

8. A process according to any one of the claims 1-4, characterized in that the liquid which is not an aromatic alcohol is water.

9. A process according to any one of the claims 1-4, characterized in that the mixture of solvents used for preparing the solution of the polymer comprises resorcinol and water.

10. A process according to claim 9, characterized in that the weight ratio of resorcinol to water is in the range of from 2:1 to 5:1.

Patentansprüche

1. Verfahren zur Herstellung von Fasern mit hoher Zugfestigkeit und hohem Modul aus einem linearen alternierenden Polymer aus Kohlenmonoxid und Ethylen mit einem geschätzten Molekulargewicht von

mindestens 100 000 g/Mol, dadurch gekennzeichnet, dass

- eine Lösung des Polymeren in einer Mischung von Lösungsmitteln, von denen mindestens eines ein aromatischer Alkohol, der frei von Alkylrestsubstituenten am aromatischen Kern ist, und das andere eine von aromatischem Alkohol sich unterscheidende Flüssigkeit ist, mit einer Extrusionsgeschwindigkeit von mindestens 1 m/min zu einem geformten, Lösungsmittel enthaltenden Gebilde extrudiert wird,
- das Gebilde durch Abkühlen oder Koagulieren in einem Nichtlösungsmittel für das Polymer verfestigt und das Lösungsmittel daraus durch Extraktion mit einem Nichtlösungsmittel für das Polymer, das in der Lösungsmittelmischung löslich ist, entfernt wird, worauf
- das Gebilde bei einer Temperatur von mindestens 180 °C verstreckt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Gebilde mit einem Abzugsverhältnis von mindestens 10 verstreckt wird.

3. Verfahren nach einem der Ansprüche 1-2, dadurch gekennzeichnet, dass die Spinnlösung in einem Luftspaltspinnverfahren zu einer Faser versponnen wird.

4. Verfahren nach einem der Ansprüche 1-3, dadurch gekennzeichnet, dass die Extrusionsgeschwindigkeit mindestens 3 m/min beträgt.

5. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass die Mischung der Lösungsmittel enthält: (a) Ethylencarbonat oder Propylencarbonat und (b) einen aromatischen Alkohol, wobei das (a):(b)-Gewichtsverhältnis im Bereich von 1:1 bis 19:1 liegt.

6. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass der aromatische Alkohol Resorcin ist.

7. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass die Flüssigkeit, die kein aromatischer Alkohol ist, Aceton ist.

8. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass die Flüssigkeit, die kein aromatischer Alkohol ist, Wasser ist.

9. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass die zur Herstellung der Lösung verwendete Mischung von Lösungsmitteln Resorcin und Wasser enthält.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, dass das Gewichtsverhältnis von Resorcin zu Wasser im Bereich von 2:1 bis 5:1 liegt.

Revendications

1. Un procédé de fabrication d'une fibre de haute résistance à la traction et de module élevé à partir d'un polymère linéaire alterné de monoxyde de carbone et d'éthylène présentant un poids moléculaire estimé au moins égal à 100 000 g/mole, caractérisé en ce que:
   - une solution du polymère dans un mélange de solvants, dont au moins l'un d'entre eux est un alcool aromatique exempt de substituants alkyle sur le noyau aromatique et un autre d'entre eux est un liquide différent d'un alcool aromatique, est extrudée en un article conformé contenant du solvant à une vitesse d'extrusion au moins égale à 1 mètre/minute;
   - l'article est solidifié par refroidissement ou par coagulation dans un non-solvant pour le polymère, et le solvant en est éliminé par extraction à l'aide d'un non-solvant pour le polymère qui est soluble dans le mélange de solvants; et ensuite
   - l'article est étiré à une température d'au moins 180 °C.

2. Un procédé selon la revendication 1, caractérisé en ce que l'article est étiré à un rapport d'étirage au moins égal à 10.

3. Un procédé selon l'une quelconque des revendications 1 à 2, caractérisé en ce que la solution de filage est filée en une fibre dans un procédé de filage traversant un espace d'air.

4. Un procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la vitesse d'extrusion est au moins égale à 3 mètres par minute.

5. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le mélange de solvants comprend:
   (a) du carbonate d'éthylène ou du carbonate de propylène; et
   (b) un alcool aromatique et le rapport pondéral (a)/(b) est de 1/1 à 19/1.

6. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'alcool aromatique est le résorcinol.

7. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le liquide qui n'est pas un alcool aromatique est l'acétone.

8. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le liquide qui n'est pas un alcool aromatique est l'eau.

9. Un procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le mélange de solvants utilisé pour préparer la solution du polymère comprend du résorcinol et de l'eau.

10. Un procédé selon la revendication 9, caractérisé en ce que le rapport pondéral du résorcinol à l'eau est de 2/1 à 5/1.